

# Non-Kramers degeneracy and oscillatory tunnel splittings in the biaxial Spin System

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## Abstract

We have investigated analytically quantum tunneling of large spin in the biaxial spin system with the magnetic field applied along the hard and medium anisotropy axes by using a purely quantum-mechanical approach. When the magnetic field parallels the hard axis, the tunnel splittings of all the energy level pairs are oscillatory as a function of the magnetic field. The quenching points are completely determined by the coexistence of solutions of the Ince's equation. When the magnetic field points the medium axis, the tunnel splitting oscillations disappear due to no coexistence of solutions. These results coincide the recent experimental observations in the nanomagnet Fe<sub>8</sub>.

In recent years much attention has been paid to quantum tunneling of magnetization (large spin) in nanomagnets, both from experiment and from theory [1]. Several magnetic particles have been identified as promising candidates for the observation of such macroscopic quantum phenomena, where the magnetization (or the Néel vector) tunnels from one potential minimum to another one. The excellent examples that have widely studied are the molecular nanomagnets Fe<sub>8</sub> [2-5] and Mn<sub>12</sub> [6-8], which have the well-defined structures and magnetic properties. On the one hand, these phenomena are very interesting from a fundamental point of view because they extend our understanding of the transition between quantum and classical behavior. On the other hand, tunneling of the magnetization changes the magnetic properties of the nanomagnets, which has the potential application for the data storage technology, e.g., making qubits - the elements of quantum computers.

Recently Wernsdorfer and Sessoli [9] have observed a novel phenomenon, i.e. oscillations of tunnel splittings of the ground and excited states in the nanomagnet Fe<sub>8</sub> described well by the spin Hamiltonian [2-5]

$$\mathcal{H} = AS_x^2 - BS_y^2 - g\mu_B \mathbf{S} \cdot \mathbf{H}, \quad (1)$$

where  $\mathbf{S}$  is a spin operator,  $\mathbf{H}$  is the magnetic field applied in the x-z plane, the spin quantum number  $s = 10$ ,  $A \approx 0.092\text{K}$ ,  $B \approx 0.229\text{K}$ ,  $g \approx 2$  is the  $g$ -factor,  $\mu_B$  is the Bohr magneton. The zero-field Hamiltonian has a biaxial symmetry with hard, easy and medium axes along x, y and z, respectively. When  $\mathbf{H}$  rotates from  $\mathbf{x}$  to  $\mathbf{z}$  direction, the oscillations of tunnel splittings of all the level pairs gradually disappear.

In fact, oscillation of the ground state tunnel splitting  $\Delta E_s$  of the model (1) with the magnetic field  $H_x$  ( $\mathbf{H} \parallel \mathbf{x}$ ) was predicted by using instanton technique [10]. The tunneling of spin is quenched when

$$h = h^*(1 - \frac{n}{s} - \frac{1}{2s}), \quad n = 0, 1, \dots, 2s - 1. \quad (2)$$

Here,  $h = \frac{H_x}{H_c}$ ,  $H_c = \frac{2s(A+B)}{g\mu_B}$  is the critical field at which the energy barrier vanishes,  $-h^* < h < h^* = \sqrt{\frac{A}{A+B}}$ , and  $s$  is an integer or half odd integer. This kind of topological quenching is the result of quantum interference of different instanton paths within the context of macroscopic quantum tunneling [11, 12], and need not be related to Kramers's degeneracy. Up to the first order of the rate  $\frac{B}{A+B}$ , the formula (2) was rederived by quantum-mechanical perturbation theory [13]. Very recently, Garg extended his previous work [10] to the excited states by using a discrete Wentzel-Kramers-Brillouin approach [14]. To order  $s^{-1}$ , the quenching points for the excited state pairs are the same as those for the ground state pair. With increasing the magnetic field, the quenching points gradually decrease and finally disappear. These results were also obtained by the potential field description of spin systems with exact spin-coordinate correspondence [15] and the instant technique [16, 17]. Because quantum tunneling of spin in the nanomagnets was observed at very low temperatures, the quantization of spin levels becomes very important to explain well the experiments. In essence, the energy spectrum of the spin systems can help us to understand the mechanism of spin tunneling thoroughly. In this paper, we have analytically diagonalized the Hamiltonian (1) in the framework of the Schrödinger's picture of quantum mechanics. The energy spectrum of the spin model is obtained in the large- $s$  limit. It is clearly shown that when  $\mathbf{H} \parallel \mathbf{x}$ , the tunnel splittings of the ground and excited state pairs are oscillatory as a function of  $H_x$  and the quenching points agree with the numerical simulation of model (1). When  $\mathbf{H} \parallel \mathbf{z}$ , the tunnel splitting oscillations of all the energy level pairs disappear, which coincided

with those obtained by the phase space path integral [18]. These phenomena have also been observed in the experiments [9, 19].

Let  $E$  and  $\Phi_m$  be the eigenenergies and eigenstates of  $\mathcal{H}$ , respectively, then the eigenvalue equation in the basis  $|s, m\rangle_z$  reads

$$u_{m-1}\Phi_{m-2} + u_{m+1}\Phi_{m+2} - t_{m-\frac{1}{2}}\Phi_{m-1} - t_{m+\frac{1}{2}}\Phi_{m+1} + \{-E + \frac{1}{2}(A+B)[s(s+1) - m^2] - g\mu_B H_z m\}\Phi_m = 0, \quad (3)$$

where

$$u_{m\pm 1} = \frac{1}{4}(A+B)\sqrt{[s(s+1) - (m\pm 1)^2]^2 - (m\pm 1)^2},$$

$$t_{m\pm\frac{1}{2}} = \frac{1}{2}g\mu_B H_x \sqrt{s(s+1) - (m - \frac{1}{2})^2 + \frac{1}{4}}$$

. Obviously, it is very difficult to strictly solve the equation (3) for arbitrary  $s$ . However, in the large- $s$  limit, Eq. (3) becomes [20]

$$(1-x^2)\frac{d^2\Phi}{dx^2} - 2x\frac{d\Phi}{dx} + [-\frac{E}{A+B} - \frac{1}{4} - \frac{1}{4}\frac{1}{1-x^2} + \frac{As(s+1)}{A+B}(1-x^2) - \frac{g\mu_B H_z \sqrt{s(s+1)}}{A+B}x - \frac{g\mu_B H_x \sqrt{s(s+1)}}{A+B}\sqrt{1-x^2}]\Phi = 0. \quad (4)$$

Here,  $x = \frac{m}{\sqrt{s(s+1)}}$  and only the leading terms are remained, i.e.  $O(s^{-1})$ . In deriving Eq. (4), we have used

$$\begin{aligned} u_{m\pm 1}\Phi_{m\pm 2} &= u_{m\pm 1}[\Phi_{m\pm 1} \pm \frac{\Phi'_{m\pm 1}}{\sqrt{s(s+1)}} + \frac{\Phi''_{m\pm 1}}{2s(s+1)} + \dots] \\ &= u\Phi \pm \frac{1}{\sqrt{s(s+1)}}\frac{d}{dx}(u\Phi) + \frac{1}{2s(s+1)}\frac{d^2}{dx^2}(u\Phi) + \dots \\ &\quad \pm \frac{1}{\sqrt{s(s+1)}}[u\frac{d\Phi}{dx} \pm \frac{1}{\sqrt{s(s+1)}}\frac{d}{dx}(u\frac{d\Phi}{dx}) + \dots] \end{aligned}$$

$$\begin{aligned}
& + \frac{u}{2s(s+1)} \frac{d^2\Phi}{dx^2} + \dots, \\
t_{m\pm\frac{1}{2}}\Phi_{m+1} &= t_{m\pm\frac{1}{2}} \left[ \Phi_{m\pm\frac{1}{2}} \pm \frac{\Phi'_{m\pm\frac{1}{2}}}{2\sqrt{s(s+1)}} + \dots \right] \\
&= t\Phi \pm \frac{1}{2\sqrt{s(s+1)}} \frac{d}{dx}(t\Phi) + \dots \\
&\quad \pm \frac{t}{2\sqrt{s(s+1)}} \frac{d\Phi}{dx} + \dots,
\end{aligned}$$

where

$$\begin{aligned}
u &= \frac{1}{4}(A+B) \left[ \sqrt{s^2(s+1)^2(1-x^2)^2 - s(s+1)x^2} \right. \\
&\approx \left. \frac{1}{4}(A+B) [s(s+1)(1-x^2) - x^2/[2(1-x^2)]] \right]
\end{aligned}$$

and  $t \approx \frac{1}{2}g\mu_B H_x \sqrt{s(s+1)} \sqrt{1-x^2}$  for large  $s$ .

Taking the transformations:  $\Phi = (1-x^2)^{-\frac{1}{4}}y(x)$  and  $x = \sin(2t)$ , and substituting them into Eq. (4), we finally obtain the Hill's equation [21]

$$\frac{d^2y}{dt^2} + [\Lambda + (a-b)\cos(2t) + (c-b)\sin(2t) + \frac{b^2}{8}\cos(4t)]y = 0, \quad (5)$$

where

$$\begin{aligned}
\Lambda &= \frac{-4E + 2As(s+1)}{A+B}, a = b - \frac{4g\mu_B H_x \sqrt{s(s+1)}}{A+B}, \\
b &= \pm 4\sqrt{\frac{As(s+1)}{A+B}}, c = b - \frac{4g\mu_B H_z \sqrt{s(s+1)}}{A+B}. \quad (6)
\end{aligned}$$

Up to now, we have mapped the spin problem (1) onto a particle problem (5). The energy spectrum of  $\mathcal{H}$  is completely determined by the characteristic levels of the Hill's equation. We note that when  $A = 0$  and  $\mathbf{H} = 0$ ,  $\Delta = m^2$ . So  $E = -B(\frac{m}{2})^2$  are nothing but the eigenvalues of the Hamiltonian (1) with integer  $s$  for even  $m$  or with half odd integer  $s$  for odd  $m$ .

For Eq. (5), there exist two monotonically increasing sequences of real numbers  $a_0, a_{2i}, b_{2i}, a'_{2i-1}$  and  $b'_{2i-1}$  ( $i = 1, 2, \dots$ ) such that Eq. (5) has a solution with period  $\pi$  if and only if  $\Lambda = a_0, a_{2i}$  or  $b_{2i}$ , and a solution with

period  $2\pi$  if and only if  $\Lambda = a'_{2i-1}$  or  $b'_{2i-1}$ . The  $a_0, a_{2i}, b_{2i}, a'_{2i-1}$  and  $b'_{2i-1}$  satisfy inequalities:

$$a_0 < b'_1 \leq a'_1 < b_2 \leq a_2 < b'_3 \leq a'_3 < b_4 \leq a_4 < \dots \quad (7)$$

According to the relation between  $E$  and  $\Lambda$  in Eq. (6), it is easy to see that the ground state of  $\mathcal{H}$  corresponds to the allowed highest characteristic level of the Hill's equation with period  $\pi$  or  $2\pi$ , depending on integer or half odd integer spin  $s$ . The lower the characteristic level of Eq. (5) is, the higher the associated eigenstate of the Hamiltonian (1) is. The tunnel splitting of the characteristic level pair of Eq. (5) with period  $\pi$  is

$$\Delta\Lambda_{2i} = a_{2i} - b_{2i}, \quad (8)$$

and the tunnel splitting of the characteristic level pair of Eq. (5) with period  $2\pi$  is

$$\Delta\Lambda'_{2i-1} = a'_{2i-1} - b'_{2i-1}. \quad (9)$$

The tunnel splitting of the energy level pair of the Hamiltonian (1) can be evaluated by the tunnel splitting of its associated characteristic level pair using Eq.(6). We note that when two of three parameters  $A$ ,  $H_x$  and  $H_z$  vanish, the Hill's equation (5) becomes the well-known Mathieu equation [22]. So the tunnel splittings of all the energy level pairs of the Hamiltonian (1) are monotonous increasing rather than oscillatory in the three cases [20]. For arbitrary parameters  $A$ ,  $B$ ,  $H_x$  and  $H_z$ , it is difficult to solve analytically Eq. (5). Here we only consider the following two special cases.

(i)  $H_z = 0$  (i.e.  $c = b$ ). In this case, Eq. (5) reduces to the Ince's equation, which has been studied in a set of literature due to its physically basic importance [21]. To observe the oscillations of tunnel splittings of model (1), we must find some vanishing points at which its eigenstates are degenerate, i.e.  $a_{2i} = b_{2i}$  or  $a'_{2i-1} = b'_{2i-1}$ . This is equivalent to find the coexistence of solutions of the Ince's equation, which means that there exist two linearly independent solutions (one even and one odd) with period  $\pi$  or  $2\pi$ . Very fortunately, due to the positive coefficient of the last term  $\cos(4t)$ , the Ince's equation has the coexistence of solutions [21] with period  $\pi$  when

$$a = -2nb \quad (10)$$

and with period  $2\pi$  when

$$a = -(2n - 1)b, \quad (11)$$

where  $n = 0, \pm 1, \pm 2, \dots$ . Obviously, the quenching points of tunnel splittings of the characteristic level pairs with period  $\pi$  are exactly shifted by half a period relative to those with period  $2\pi$ . Under the conditions (10) and (11), the Ince's equation becomes the Whittaker equation [21]

$$\frac{d^2 y}{dt^2} + [\Lambda - p b \cos(2t) + \frac{b^2}{8} \cos(4t)] y = 0. \quad (12)$$

Here,  $p = 2n + 1$  or  $2n$  for Eq. (10) or (11), respectively. For Eq. (12), when  $b \rightarrow 0$ , then  $a_0 \rightarrow 0$ ,  $a_{2i}$  and  $b_{2i} \rightarrow (2i)^2$ , and  $a'_{2i-1}$  and  $b'_{2i-1} \rightarrow (2i-1)^2$  [23].

*Integer spin  $s$ .* Due to Eq. (6), the eigenstates of the Hamiltonian (1) correspond to the characteristic levels of the Ince's equation with period  $\pi$ , i.e.  $E_0^a = -\frac{1}{4}(A+B)a_0 + E_0$ ,  $E_i^a = -\frac{1}{4}(A+B)a_{2i} + E_0$  and  $E_i^b = -\frac{1}{4}(A+B)b_{2i} + E_0$ ,  $E_0 = \frac{1}{2}As(s+1)$ ,  $i = 1, 2, \dots, s$ . So the tunnel splitting of the energy level pair  $(E_i^a, E_i^b)$  is

$$\Delta E_i = E_i^b - E_i^a = \frac{1}{4}(A+B)\Delta\Lambda_{2i}. \quad (13)$$

From Eq. (10), we have  $\Delta E_i = 0$  when

$$H_x = \frac{(2n+1)\sqrt{A(A+B)}}{g\mu_B}. \quad (14)$$

The existence of the quenching fields (14) clearly shows that the tunnel splittings of all the energy levels of  $\mathcal{H}$  are oscillatory as a function of  $H_x$  and the period of oscillations  $\Delta H = \frac{2\sqrt{A(A+B)}}{g\mu_B}$ . This coincides with Garg's result (2) [10, 14]. For Eq. (12), when  $|p| = 2l + 1$ , then the even intervals of instability on the  $\Lambda$  axis disappear with at most  $l + 1$  exceptions [21]. In other words, the characteristic values  $a_0, a_{2i}$  and  $b_{2i}$  satisfy

$$\begin{aligned} a_0 &< b_2 < a_2 < \dots < b_{2l} < a_{2l} \\ &< b_{2(l+1)} = a_{2(l+1)} < \dots < b_{2s} = a_{2s}. \end{aligned} \quad (15)$$

This means that the tunnel splittings of the  $l$  highest excited state pairs of the Hamiltonian (1) do not vanish while those of the other  $s-l$  energy level pairs vanish. With increasing the magnetic field  $H_x$  (i.e.  $|p|$ ), the quenching points gradually decrease and finally disappear when  $l \geq s$ . The configuration of

the quenching points agree with that from the numerical simulation of the Hamiltonian (1) (see Fig. 1).

*Half odd integer spin  $s$ .* The eigenstates of the Hamiltonian (1) correspond to the characteristic levels of Eq. (12) with period  $2\pi$ , i.e.  $E_{i-\frac{1}{2}}^{a'} = -\frac{1}{4}(A+B)a'_{2i-1} + E_0$  and  $E_{i-\frac{1}{2}}^{b'} = -\frac{1}{4}(A+B)b'_{2i-1} + E_0, i = 1, 2, \dots, s + \frac{1}{2}$ . The tunnel splitting of the energy level pair  $(E_{i-\frac{1}{2}}^{a'}, E_{i-\frac{1}{2}}^{b'})$  reads

$$\Delta E'_{i-\frac{1}{2}} = E_{i-\frac{1}{2}}^{b'} - E_{i-\frac{1}{2}}^{a'} = \frac{1}{4}(A+B)\Delta\Lambda'_{2i-1}. \quad (16)$$

According to Eq. (11), we obtain  $\Delta E'_{i-\frac{1}{2}} = 0$  when

$$H'_x = \frac{2n\sqrt{A(A+B)}}{g\mu_B}. \quad (17)$$

Obviously, the period of oscillations of tunnel splittings for all the energy level pairs  $(E_{i-\frac{1}{2}}^{a'}, E_{i-\frac{1}{2}}^{b'})$  is  $\Delta H' = \frac{2\sqrt{A(A+B)}}{g\mu_B}$ , which is the same with that of the energy level pairs  $(E_i^a, E_i^b)$ . However, the quenching points for half odd integer spin  $s$  are shifted half a period (i. e.  $\frac{\sqrt{A(A+B)}}{g\mu_B}$ ) relative to those for integer spin  $s$ . For Eq. (12), if  $|p| = 2l$ , then at most  $l + 1$  odd interval of instability on the  $\Lambda$  axis remain, i. e.

$$\begin{aligned} b'_1 < a'_1 < b'_3 < a'_3 < \dots < b'_{2l-1} < a'_{2l-1} \\ < b'_{2l+1} = a'_{2l+1} < \dots < b'_{2s} = a'_{2s}. \end{aligned} \quad (18)$$

It is easy to see that the tunnel splittings of the  $s - l + \frac{1}{2}$  lowest energy level pairs vanish, but the tunnel splittings of the other  $l$  highest energy level pairs do not. When  $l > s - \frac{1}{2}$ , there do not exist the quenching points. These results also coincide with those obtained by the discrete WKB approach [14].

(ii)  $H_x = 0$  (i.e.  $a = b$ ). Let  $t \rightarrow t + \frac{\pi}{4}$ , then Eq. (5) becomes the Ince's equation

$$\frac{d^2 y}{dt^2} + [\Lambda + (c - b)\cos(2t) - \frac{b^2}{8}\cos(4t)]y = 0. \quad (19)$$

Because the coefficient of the last term  $\cos(4t)$  is negative, Eq. (19) does not possess the coexistence of solutions, i.e. two linearly independent solutions

[21]. This means that the sign of equality in the inequalities (7) cannot hold and each energy level of  $\mathcal{H}$  is singlet in the parameter space. So the tunnel splittings of all the level pairs are not oscillatory with  $H_z$ , which coincide the experiment [9, 19].

In conclusion, we studied quantum tunneling of large spin in the biaxial spin systems by using quantum mechanics. The energy spectrum of the spin model (1) is obtained by solving Hill's equation (5), which is derived directly from the eigenvalue equation of the spin problem in the large- $s$  limit. It is surprising that when  $\mathbf{H} \parallel \mathbf{x}$ , the vanishing points of the tunnel splittings of all the energy level pairs obtained here by the coexistence of solutions of the Ince's equation coincide those given by the WKB method [10, 14] and other approaches [15-17]. However, our approach is a natural way of explaining the oscillations of tunnel splitting in the biaxial spin system, which is also applied in other spin Hamiltonians.

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Fig. 1 The exact quenching points of all the level pairs of the Hamiltonian (1) with  $s = 10$ ,  $A = 0.092K$ ,  $B = 0.229K$ , and  $H_z = 0$ .

